

# (H<sub>2</sub>NC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)[(VO)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>] and (H<sub>2</sub>NC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[(VO)<sub>3</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>]·H<sub>2</sub>O: Novel Layered Vanadium Phosphates with Distorted and Defected VOPO<sub>4</sub> Layers

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Two new layered vanadium phosphates, (H<sub>2</sub>NC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)[(VO)(PO<sub>4</sub>)<sub>2</sub>] (1) and (H<sub>2</sub>NC<sub>4</sub>H<sub>8</sub>NH<sub>2</sub>)<sub>2</sub>[(VO)<sub>3</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>]·H<sub>2</sub>O (2), have been hydrothermally synthesized under similar conditions. Compound 1 is synthesized from VCl<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, piperazine, (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NOH, and H<sub>2</sub>O in the mole ratio 1:2.7:2.1:1.2:350 at 200 °C for 70 h and autogeneous pressure. In contrast, the preparation of 2 required the presence of (CH<sub>3</sub>)PO<sub>3</sub>H<sub>2</sub>, such that reaction of VCl<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, (CH<sub>3</sub>)PO<sub>3</sub>H<sub>2</sub>, piperazine (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NOH, and H<sub>2</sub>O in the mole ratio 1:3.5:1.2:3.3:1.2:390 at 200 °C for 70 h yields 2 in 50% yield, with 1 as the other component. Green plates of compound 1 crystallize in the monoclinic space group *P*2<sub>1</sub>/*c* with *a* = 8.786(2) Å, *b* = 8.257(2) Å, *c* = 8.566(2) Å, β = 111.07(3)°, *V* = 579.9(3) Å<sup>3</sup>, *Z* = 2, and *R* = 0.0298 whereas blue plates of 2 crystallize in the noncentrosymmetric orthorhombic space group *Pna*2<sub>1</sub> with *a* = 14.631(3) Å, *b* = 8.706(2) Å, *c* = 17.635(4) Å, *V* = 2246.3(11) Å<sup>3</sup>, *Z* = 4, and *R* = 0.0363. Compound 1 has puckered layers containing triangular bipyramidal vanadium(IV) centers. Phosphate 2 has VOPO<sub>4</sub>-like layers with 1/4 of the V(IV) octahedral sites missing which results in unusual edge-sharing involving half the phosphate tetrahedral with the vanadium octahedra and protonation of the remaining phosphate groups to give HPO<sub>4</sub><sup>2-</sup> residues.

## Introduction

Vanadium phosphate materials with a V/P ratio of around 1:1 are important catalysts used in the synthesis of maleic anhydride from lighter hydrocarbons.<sup>1–3</sup> One might expect that if microporous materials with catalytically active transition elements could be prepared, oxidation catalysts displaying even greater selectivities might be realized. However, if these M/P/O systems are to exhibit size and shape selective catalytic properties of zeolites and aluminophosphates,<sup>4–6</sup> structures with large pores are needed. A reasonable approach consists of using organic (instead of inorganic) molecules or cations as the templating agents that can leave large cavities or micropores when removed from the framework by either thermal or by ion-exchange methods. Hydrothermal synthesis with organic templates has afforded two- or three-dimensional (2- or 3-D) materials possessing a range of cavities, micropores, or interlayer spacings depending on the size of the templating agent. We have previously reported several 2- and 3-D Mo/P/O systems that have organic ammonium cations as the templating agent<sup>7–9</sup> and have recently extended the organically templated 3-D transition element system to vanadium phosphates.<sup>10–13</sup> Since it appears that open framework V/P/O

systems tend to favor more polar templates, such as amines and diamines, we have used piperazine in this study as the templating agent and have isolated two 2-D materials.

A large number of such 2-D layered V/P/O systems have been described previously including VO(HPO<sub>4</sub>)·xH<sub>2</sub>O,<sup>14</sup> VOPO<sub>4</sub>·xH<sub>2</sub>O,<sup>15</sup> A<sub>2</sub>VP<sub>2</sub>O<sub>8</sub> [A = K, Rb, Cs;<sup>16a–d</sup> A = Na<sup>16e</sup>] β-K<sub>2</sub>V<sub>3</sub>P<sub>4</sub>O<sub>17</sub>,<sup>16f</sup> and K<sub>2</sub>[(V<sup>IV</sup>O)<sub>2</sub>V<sup>III</sup>(PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>].<sup>16g</sup> Layered compounds with alternating inorganic/organic layers, such as the vanadium phosphates reported here, have been obtained by intercalation of the organic species into an inorganic host lattice, for example, amines intercalated into clays,<sup>17</sup> organoammonium cations into transition-metal oxides and dichalcogenides,<sup>18</sup> or redox intercalation into VOPO<sub>4</sub>·xH<sub>2</sub>O lattices.<sup>19</sup> Examples of the direct incorporation of the organic moiety are found in zirconium or

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- (1) Hodnett, B. L. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 373.
- (2) Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55.
- (3) Bordes, E.; Courtine, P. *J. Catal.* **1979**, *57*, 236.
- (4) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: New York, 1982.
- (5) Occelli, M. L.; Robson, H. E. *Zeolite Synthesis*; American Chemical Society: Washington, DC, 1989.
- (6) Szostak, R. *Molecular Sieves Principles of Synthesis and Identification*; Van Nostrand Reinhold: New York, 1989.
- (7) Mundi, L. A.; Strohmaier, K. G.; Haushalter, R. C. *Inorg. Chem.* **1991**, *30*, 153.
- (8) Meyer, L. A.; Haushalter, R. C. *Inorg. Chem.* **1993**, *32*, 1579.
- (9) Review: Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.
- (10) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596.
- (11) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610.
- (12) (NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>)K[(VO)(PO<sub>4</sub>)<sub>2</sub>]; Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1993**, *5*, 1595.

(13) (NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>)(VO)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>; Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1993**, *5*, 1595.

(14) Le Bail, A.; Ferey, G.; Amoros, P.; Beltran-Porter, D. *Eur. J. Solid State Inorg. Chem.* **1989**, *26*, 419. Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, H. F., Jr.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370.

(15) Tietze, H. R. *Aust. J. Chem.* **1981**, *34*, 2035. Tachez, M.; Theobald, F.; Bernard, J.; Hewat, A. W. *Rev. Chim. Miner.* **1982**, *19*, 291.

(16) (a) Gurbunova, Yu. E.; Linde, S. A.; Lavrov, A. V.; Tananaev, I. V. *Dokl. Akad. Nauk SSSR* **1980**, *250*(2), 350. (b) Hoard, J. L.; Sullenger, D. B.; Kennard, C. H. L.; Hughes, R. E. *J. Solid State Chem.* **1970**, *1*, 268. (c) Andersson, S.; Lungstrom, T. *J. Solid State Chem.* **1970**, *2*, 603. (d) Lii, K. H.; Wang, S. L. *J. Solid State Chem.* **1989**, *82*, 239. (e) Benhamada, L.; Grandin, A.; Borel, M. M.; Leclaire, A.; Raveau, B. *J. Solid State Chem.* **1992**, *101*, 154. (f) Lii, K. H.; Tsai, H. J.; Wang, S. L. *J. Solid State Chem.* **1990**, *87*, 396. Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J.; O'Connor, C. J. Submitted for publication.

(17) Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982. Dines, M. B.; Marrocco, M. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 2, pp 1–57. Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: New York, 1978. Thomas, J. M.; Adams, J. M.; Tennakoon, D. T. B. *Adv. Chem. Ser.* **1977**, *No. 163*, 298–315.

(18) Schöllhorn, R.; Schulte-Nolle, T.; Steinhoff, G. *J. Less-Common Met.* **1980**, *71*, 71. Schöllhorn, R.; Klein Reesink, F.; Reimold, R. *J. Chem. Soc., Chem. Commun.* **1979**, 398. Subba Rao, G. V.; Shafer, M. W. In *Intercalated Layered Materials*; Levy, F., Ed.; D. Reidel Publishing Co.; Dordrecht, 1979; pp 990–199. Schöllhorn, R. *Solvated Intercalation Compounds of Layered Chalcogenide and Oxide Bronzes*. In Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982; pp 315–360.

vanadium organophosphonates and organophosphates which were obtained hydrothermally or by simple precipitation from aqueous solutions.<sup>20</sup> We have prepared the title compounds  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)[(\text{VO})_2(\text{PO}_4)_2]$  (**1**) and  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_1(\text{PO}_4)_2]\cdot 2\text{H}_2\text{O}$  (**2**) hydrothermally, with direct incorporation of the organic dication, piperazinium, during the synthesis yielding 2-D layered vanadium(IV) phosphates.

### Experimental Section

The hydrothermal reactions were run in Parr acid digestion bombs with 23 mL poly(tetrafluoroethylene) liners. The  $\text{H}_3\text{PO}_4$  (85 wt % solution),  $(\text{CH}_3)_3\text{PO}_3\text{H}_2$ , piperazine,  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$  (40 wt % solution), and  $\text{VCl}_4$  were obtained from Aldrich and the  $\text{V}_2\text{O}_5$  and V metal (-325 mesh) from Cerac. The  $\text{VCl}_4$  was carefully hydrolyzed to generate a turquoise solution of "VO<sup>2+</sup>" that was used as the vanadium(IV) source. In a typical preparation, 5 mL of  $\text{VCl}_4$  was syringed into a flask cooled to 4 °C and 20 mL of  $\text{H}_2\text{O}$  added dropwise over a period of 0.5 h. **Caution:** Care should be taken during hydrolysis as the reaction is exothermic and generates HCl gas. Single-crystal X-ray diffraction was performed on a Rigaku AFC5S. Powder X-ray patterns were recorded on an XDS 2000 Scintag diffractometer while infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR spectrometer. Thermogravimetric analysis was done on a Perkin-Elmer TGA 7 under nitrogen atmosphere with a heating rate of 10 deg min<sup>-1</sup>.

**Synthesis of  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)[(\text{VO})_2(\text{PO}_4)_2]$  (**1**).** Phosphate **1** was prepared from the reaction of  $\text{VCl}_4$ ,  $\text{H}_3\text{PO}_4$ , piperazine, *tert*-butyl ammonium hydroxide, and  $\text{H}_2\text{O}$  in the molar ratio of 1:2.7:2.1:1.2:350 (mass of  $\text{VCl}_4 = 0.2724$  g) heated at 200 °C for 70 h. After the product was washed with water several times and air-dried **1** is obtained as monophasic material in 56% yield (based on the total amount of "V<sup>4+</sup>" used). The composition was confirmed by the comparison of the powder pattern with the simulated one. IR (KBr pellet, cm<sup>-1</sup>): 3100, 1610, 1386 (vs), 1118, 994, and 651.

**Synthesis of  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2]\cdot 2\text{H}_2\text{O}$  (**2**).** Phosphate **2** is synthesized under the same conditions of temperature and reaction time but with the required addition of  $(\text{CH}_3)_3\text{PO}_3\text{H}_2$  to the reaction mixture. The reaction of  $\text{VCl}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $(\text{CH}_3)_3\text{PO}_3\text{H}_2$ , piperazine,  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$ , and  $\text{H}_2\text{O}$  in the mole ratio 1:3.5:1.2:3.3:1.2:390 (mass of  $\text{VCl}_4$  of 0.2724 g) gave **2** in 50% yield. These represent optimal reaction ratios and under no conditions could **2** be synthesized as a monophasic material free of **1** in variable amounts. IR (KBr pellet, cm<sup>-1</sup>): 3032, 1593 (s), 1383 (vs), 1041 (s), 963. Attempts to increase the yields of **2** by varying the mole ratios and starting materials resulted in the formation of an additional as yet unidentified, microcrystalline material, A, which was obtained as a single phase when  $\text{V}_2\text{O}_5$ , V,  $\text{H}_3\text{PO}_4$ , piperazine, and  $\text{H}_2\text{O}$  were reacted in the mole ratio of 1.2:1:5.0:6.7:1560 (mass of V = 0.0199 g) at 200 °C for 93 h. IR (KBr pellet, cm<sup>-1</sup>): 3517, 3030 (s), 2808, 1607 (s), 1463 (m), 1380 (m), 1048 (vs), 992 (vs) cm<sup>-1</sup>.

**Synthesis of  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2(\text{H}_2\text{NC}_3\text{H}_7)_2[\text{H}_4\text{PV}_{14}\text{O}_{42}]$  (**3**).** Compound **1** (0.088 g) was added to a solution of piperidine (0.21 mL) in aqueous HCl (5 mL, pH 5), and this mixture was heated in a Teflon-lined bomb at 68 °C for 138 h. The resultant mixture of brown needles of **3** and unreacted **1** was collected and added to a solution of piperidine (0.1 mL) in  $\text{H}_2\text{O}$  (4 mL) and HCl (1.22 N, 0.85 mL), which was heated at 68 °C for 234 h. Yield of crystalline **3** was 0.0312 g. The identity of **3** was confirmed by X-ray crystallography. Since the material contains a known molecular anion, no further investigations were carried out.

**Crystallography.** For compounds **1** and **2**, the details of the crystal data, data collection, and solution<sup>21-24</sup> and refinement are summarized in Table 1, atomic coordinates and equivalent isotropic displacement

**Table 1.** Crystal Parameters for the Structure Determination of  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)[(\text{VO})_2(\text{PO}_4)_2]$  (**1**) and  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2]\cdot 2\text{H}_2\text{O}$  (**2**)

	1	2
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$ , No. 14	$Pna2_1$ , No. 33
<i>a</i> , Å	8.786(2)	14.631(3)
<i>b</i> , Å	8.257(2)	8.706(2)
<i>c</i> , Å	8.566(2)	17.635(4)
$\beta$ , deg	111.07(3)	
<i>V</i> , Å <sup>3</sup>	579.9(3)	2246.3(11)
<i>Z</i>	2	4
<i>D</i> , calc	2.359	2.280
$\mu$ , cm <sup>-1</sup>	19.44	16.13
<i>F</i> (000)	412	1564
<i>T</i> , K	296	294
reflections collected	1685	1930
reflections obsd ( $F = 6.0\sigma(F)$ )	1405	904
$R^a$	0.0298	0.0363
$R_w^b$	0.0341	0.0444

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = \sum w|F_o| - |F_c| / \sum w|F_o|.$$

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{Å}^2 \times 10^3$ ) for  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)[(\text{VO})_2(\text{PO}_4)_2]$  (**1**)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
V(1)	8426(1)	340(1)	1775(1)	7(1)
P(2)	9429(1)	-2657(1)	-204(1)	7(1)
O(1)	6627(3)	1028(3)	1405(3)	18(1)
O(2)	8541(3)	-1170(2)	113(3)	14(1)
O(3)	8228(2)	-1499(2)	3241(2)	12(1)
O(4)	8993(2)	2130(2)	451(3)	13(1)
O(5)	10122(2)	1181(2)	3711(2)	13(1)
N(1)	3589(3)	5700(3)	218(3)	14(1)
C(1)	5274(3)	6287(3)	1220(4)	16(1)
C(2)	6485(3)	4937(4)	1438(4)	16(1)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

coefficients in Tables 2 and 3, and bond lengths and angles in Tables 4 and 5. In the case of compound **2**, the acentric space group  $Pna2_1$  and the centric  $Pnam$  were consistent with the observed absences. However, attempts to refine in the centric space group resulted in numerous unsatisfactory thermal parameters and consistently poor refinement. The choice of the acentric space group is confirmed by the successful refinement of the structure and by the absence of significant correlations within the matrix. Full crystallographic details are provided in the supplementary material.

**Thermogravimetric Analysis.** Thermogravimetric analysis for **1** showed a 17% weight loss at 480 °C corresponding to loss of the piperazinium dication (calculated, 21%), whereas for **2** a loss of 19% occurred at 440 °C (calculated, 22%). For material A, we noted several weight losses: 2% at 90 °C, 2% at 130 °C, 6% at 310 °C, 3% at 420 °C, and 10% at 480 °C.

### Discussion

The V/P/O solid  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)[(\text{VO})(\text{PO}_4)]_2$  (**1**) was obtained as a monophasic material from the hydrothermal reaction of  $\text{VCl}_4$ ,  $\text{H}_3\text{PO}_4$ , piperazine,  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$ , and  $\text{H}_2\text{O}$ . Optimization of synthetic conditions revealed that  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$  was the most effective reagent in adjusting the pH of the solution from 3 to 6, a necessary condition in the formation of the title compounds. In contrast, when potassium or sodium hydroxide were used, the desired products did not form. The preparation of compound **2** required the addition of  $(\text{CH}_3)_3\text{PO}_3\text{H}_2$  to the reaction mixture and a pH of 5, in contrast to **1** which is isolated as a single phase at pH 6. Under optimized conditions, compound **2** could be obtained in 50% yield in the presence of phosphate **1**. Variations in reactant stoichiometries produced **2** as a minor

- (19) Johnson, J. W.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *5*, 412. Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842. Johnson, J. W.; Jacobson, A. J.; Rich, S. M.; Brody, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5246. Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117. Cao, G.; Hong, H.-G.; Mallouk, T. M. *Acc. Chem. Res.* **1992**, *25*, 420. Dines, M. B.; Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567. Dines, M. B.; Cooksey, R. E.; Griffith, P. C.; Lane, R. H. *Inorg. Chem.* **1983**, *22*, 1003.
- (20) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842. Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, W., Jr. *Chem. Mater.* **1990**, *2*, 91.
- (21) Calabrese, J. C., PHASE—Patterson Heavy Atom Solution Extractor, Ph.D. Thesis University of Wisconsin—Madison, 1972. Beurskens, P. T. DIRDIF—Direct Methods for Difference Structures and Automatic Procedure for Phase Extraction and Refinement of Difference Structure Factors, Technical Report 1984/1; Crystallographic Laboratory: Toer-noiveld, 6525 Ed Nijmegen, The Netherlands.

- (22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.A.
- (23) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
- (24) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

**Table 3.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
V(1)	6507(1)	-4389(2)	4012(1)	12(1)
V(2)	8110(1)	620(2)	3919	12(1)
V(3)	6778(1)	167(2)	6523(2)	12(1)
P(1)	2239(2)	1475(3)	3019(2)	13(1)
P(2)	2429(2)	6524(4)	4914(2)	12(1)
P(3)	2170(2)	2074(4)	5211(2)	12(1)
P(4)	2557(2)	2062(4)	7716(2)	14(1)
O(1)	499(5)	-1178(9)	4209(4)	19(2)
O(2)	4133(5)	3819(9)	3720(4)	20(2)
O(3)	4267(5)	269(9)	1640(4)	26(2)
O(4)	1235(5)	962(9)	3142(4)	18(2)
O(5)	2749(5)	482(9)	3593(4)	15(2)
O(6)	2534(5)	1215(10)	2201(5)	21(2)
O(7)	2337(5)	3198(9)	3196(5)	17(2)
O(8)	3436(5)	6051(9)	4730(4)	15(2)
O(9)	1887(5)	5517(9)	4378(4)	14(2)
O(10)	2781(5)	1256(10)	746(5)	17(2)
O(11)	2296(5)	-1754(9)	4749(5)	15(2)
O(12)	1440(5)	1216(9)	4746(4)	14(2)
O(13)	2897(5)	2874(9)	4751(4)	16(2)
O(14)	1700(5)	3146(9)	5754(5)	19(2)
O(15)	2679(6)	763(10)	5682(5)	28(2)
O(16)	2047(5)	3135(10)	7199(5)	25(2)
O(17)	1853(5)	1130(9)	8147(5)	18(2)
O(18)	1737(5)	-2149(9)	3202(4)	16(2)
O(19)	1869(6)	-4037(11)	2199(5)	37(2)
O(20)	1408(14)	3278(21)	1391(14)	52(5)
N(1)	176(7)	102(12)	673(6)	24(3)
N(2)	-269(7)	9819(11)	2283(6)	23(2)
N(3)	366(8)	4336(14)	9747(7)	40(3)
N(4)	-19(9)	5720(15)	8280(8)	46(3)
C(1)	701(8)	9098(14)	1194(7)	24(3)
C(2)	129(8)	8518(14)	1831(7)	26(3)
C(3)	-268(9)	11376(15)	1114(8)	32(3)
C(4)	-822(9)	10846(14)	1773(7)	29(3)
C(5)	801(6)	3808(11)	9034(6)	5(2)
C(6)	205(8)	4023(14)	8362(7)	21(3)
C(7)	130(8)	6064(15)	9652(7)	25(3)
C(8)	-463(6)	6294(10)	8974(6)	3(2)

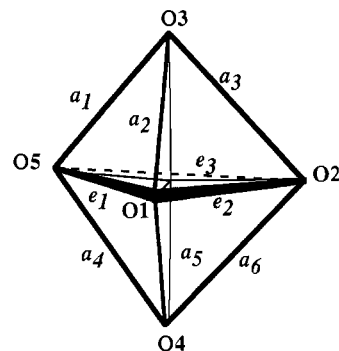
<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_2(\text{PO}_4)_2]$  (1)

V(1)-O(1)	1.600(2)	V(1)-O(2)	1.923(2)
V(1)-O(3)	2.017(2)	V(1)-O(4)	2.031(2)
V(1)-O(5)	1.918(2)	P(2)-O(2)	1.531(2)
P(2)-O(3A)	1.537(2)	P(2)-O(4A)	1.538(2)
P(2)-O(5A)	1.532(2)	O(3)-P(2C)	1.537(2)
O(4)-P(2A)	1.538(2)	O(5)-P(2B)	1.532(2)
N(1)-C(2A)	1.500(3)	N(1)-C(2A)	1.492(4)
O(1)-V(1)-O(2)	113.2(1)	O(1)-V(1)-O(3)	95.2(1)
O(2)-V(1)-O(3)	90.7(1)	O(1)-V(1)-O(4)	93.1(1)
O(2)-V(1)-O(4)	88.2(1)	O(3)-V(1)-O(4)	171.3(1)
O(1)-V(1)-O(5)	116.7(1)	O(2)-V(1)-O(5)	130.1(1)
O(3)-V(1)-O(5)	87.0(1)	O(4)-V(1)-O(5)	87.1(1)
O(2)-P(2)-O(3A)	106.4(1)	O(2)-P(2)-O(4A)	109.8(1)
O(3A)-P(2)-O(4A)	112.4(1)	O(2)-P(2)-O(5A)	110.4(1)
O(3A)-P(2)-O(5A)	109.3(1)	O(4A)-P(2)-O(5A)	108.5(1)
V(1)-O(2)-P(2)	144.9(1)	V(1)-O(3)-P(2C)	134.0(1)
V(1)-O(4)-P(2A)	134.2(1)	V(1)-O(5)-P(2B)	146.6(1)
C(1)-N(1)-C(2A)	110.8(3)	N(1)-C(1)-C(2)	109.8(2)
C(1)-C(2)-N(LA)	110.8(2)		

phase in low yield. Omission of  $(\text{CH}_3)_2\text{PO}_3\text{H}_2$  from the reaction mixture for compound 2 resulted in the formation of a third crystalline V/P/O phase, which is as yet unidentified. Minor modifications in reaction conditions result in at least two further phases which can be isolated as single-phase materials. Powder X-ray diffractograms confirm that all three additional phases are unique, while thermogravimetric analysis indicates the presence of the piperazinium template in all cases. Further investigations of these phases are in progress.

Previously, we synthesized by hydrothermal methods two 3-D vanadium phosphates which crystallized with incorporation of

**Figure 1.** Trigonal bipyramidal environment of the V(IV) centers of compound 1. The dihedral angles between the edges indicated are defined in ref 26.**Table 5.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (2)

V(1)-O(4A)	2.094(8)	V(1)-O(1A)	1.593(7)
V(1)-O(11B)	2.003(8)	V(1)-O(5A)	2.180(7)
V(1)-O(18A)	1.987(8)	V(1)-O(12A)	2.052(8)
V(2)-O(2A)	1.612(8)	V(2)-O(7A)	1.990(8)
V(2)-O(8A)	2.096(8)	V(2)-O(9A)	2.199(7)
V(2)-O(13A)	1.992(8)	V(2)-O(17A)	2.044(8)
V(3)-O(3A)	1.589(8)	V(3)-O(6A)	1.972(9)
V(3)-O(10A)	1.957(9)	V(3)-O(14A)	2.002(8)
V(3)-O(16A)	1.939(9)	P(1)-O(4)	1.552(8)
P(1)-O(5)	1.525(8)	P(1)-O(6)	1.522(9)
P(1)-O(7)	1.539(9)	P(2)-O(9)	1.514(8)
P(2)-O(8)	1.563(8)	P(2)-O(10B)	1.517(9)
P(2)-O(11A)	1.539(8)	P(3)-O(12)	1.540(8)
P(3)-O(13)	1.508(8)	P(3)-O(14)	1.505(9)
P(3)-O(15)	1.596(9)	P(4)-O(16)	1.504(9)
P(4)-O(17)	1.515(8)	P(4)-O(18B)	1.507(8)
P(4)-O(19A)	1.566(10)		
P(1A)-V(1)-O(1A)	134.9(3)	O(4A)-V(1)-O(5A)	67.9(3)
O(1A)-V(1)-O(4A)	100.7(4)	O(1A)-V(1)-O(11B)	103.8(4)
O(1A)-V(1)-O(5A)	168.6(4)	O(5A)-V(1)-O(11B)	87.5(3)
P(1A)-V(1)-O(11B)	121.2(2)	O(1A)-V(1)-O(12A)	93.4(4)
O(4A)-V(1)-O(11B)	155.5(3)	O(5A)-V(1)-O(12A)	85.1(3)
P(1A)-V(1)-O(12A)	84.7(2)	O(4A)-V(1)-O(18A)	86.9(3)
O(4A)-V(1)-O(12A)	86.9(3)	O(11B)-V(1)-O(18A)	91.9(3)
O(11B)-V(1)-O(12A)	90.2(3)	O(2A)-V(2)-O(7A)	103.4(4)
O(1A)-V(1)-O(18A)	96.0(4)	O(2A)-V(2)-O(8A)	98.5(3)
O(5A)-V(1)-O(18A)	84.8(3)	O(7A)-V(2)-O(9A)	90.3(3)
O(12A)-V(1)-O(18A)	169.6(3)	O(7A)-V(2)-O(13A)	92.4(3)
O(7A)-V(2)-O(8A)	157.7(3)	O(9A)-V(2)-O(13A)	84.1(3)
O(2A)-V(2)-O(9A)	166.3(3)	O(2A)-V(2)-O(17A)	93.2(4)
O(8A)-V(2)-O(9A)	67.8(3)	O(8A)-V(2)-O(17A)	86.1(3)
O(2A)-V(2)-O(13A)	96.1(4)	O(13A)-V(2)-O(17A)	170.1(3)
O(8A)-V(2)-O(13A)	89.4(3)	O(3A)-V(3)-O(10A)	104.9(4)
O(7A)-V(2)-O(17A)	88.5(3)	O(3A)-V(3)-O(14A)	102.0(4)
O(9A)-V(2)-O(17A)	86.1(3)	O(10A)-V(3)-O(14A)	90.5(4)
O(3A)-V(3)-O(6A)	105.5(4)	O(6A)-V(3)-O(16A)	89.4(4)
O(6A)-V(3)-O(10A)	82.5(4)	O(14A)-V(3)-O(16A)	82.4(4)
O(6A)-V(3)-O(14A)	152.5(3)		
O(3A)-V(3)-O(16A)	107.3(4)		
O(10A)-V(3)-O(16A)	147.8(3)		

the same template, the 1,3-propanediammonium dication,  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3)\text{K}[(\text{VO})_3(\text{PO}_4)_3]$  and  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2[(\text{VO})_3(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_2] \cdot 12\text{H}_2\text{O}$ .<sup>12,13</sup> In contrast, by use of the piperazinium dication, the 2-D layered vanadium phosphates **1** and **2** were obtained. In these compounds anionic inorganic V/P/O layers alternate with organic piperazinium cations. The V/P/O layers of both compounds are structurally related to the layer section of  $\text{MOXO}_4$  ( $M = \text{V}, \text{Nb}, \text{Ta}, \text{Mo}; \text{X} = \text{P}, \text{As}, \text{S}, \text{Mo}$ ) type compounds. The structure of  $\text{MoPO}_4$ ,<sup>25</sup> which is isotopic with  $\alpha\text{-IV-VOPO}_4$ , provides a prototype for discussion.

The  $\{\text{VOPO}_4\}$  layer of phosphate **1** consists of a framework of corner-sharing  $\text{VO}_5$  polyhedra and  $\text{PO}_4$  tetrahedra. The vanadium polyhedra adopt distorted triangular bipyramidal geometry, using the criteria developed by Muettterties and Guggenberger<sup>26</sup> and

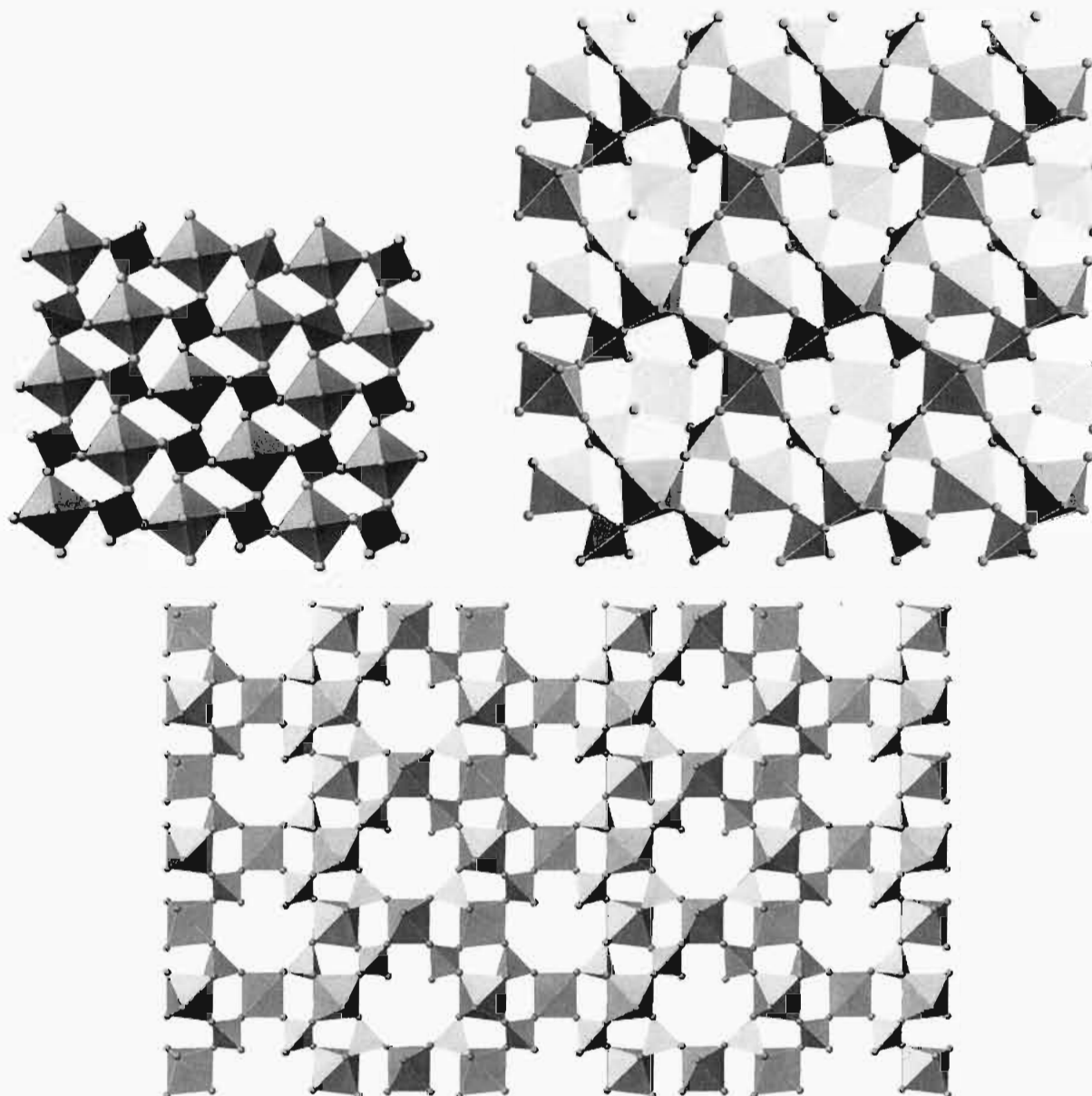


Figure 2. (a, top left) Layer structure of  $\text{MoOPO}_4$ , viewed down the crystallographic  $c$  axis. (b, top right) V-P-O layer of **1**, viewed down  $a$ . (c, bottom) A layer section of **2**, viewed down  $[100]$ .

summarized in Table 6. Figure 1 illustrates the polyhedral form of an isolated trigonal bipyramid of compound **1** with the relevant dihedral angles indicated. The vanadium center is in the +4 oxidation state, a feature consistent with bond length and bond strength calculations which give a value of 3.95 valence units.<sup>27</sup> The angles between the three oxygens forming the equatorial plane fall in the range  $113\text{--}130^\circ$ , while the angle between the axial oxygens is  $171^\circ$ . Four out of the five V-O distances are similar (1.92–2.03 Å) and typical of V-O bond lengths, whereas the fifth one is much shorter, 1.60 Å, consistent with a V=O multiple bond. The presence of triangular bipyramidal centers as opposed to octahedral centers causes distortions or puckerings of the  $\text{MOPO}_4$  layer as seen by comparing parts a and b of Figure 2. Figure 2a shows the layer section of  $\text{MoOPO}_4$ <sup>25</sup> where each  $\text{MoO}_6$  octahedron is connected to adjacent  $\text{PO}_4$  tetrahedra through corner-sharing. Figure 2b depicts a layer of compound **1** where each triangular bipyramidal vanadium center is connected to four phosphate tetrahedra by sharing corners, while the fifth bond, V1-O1, which is one of the equatorial bonds, points toward the interlamellar region. The  $\{\text{VOPO}_4\}$  layers of compound **1**

Table 6. Dihedral Angles (deg) for Idealized Trigonal Bipyramidal and Square Pyramidal Geometries and for the  $\{\text{VO}_5\}$  Sites of **1** and **2**

polygon	shape determining angles ( $e_1\text{--}e_3$ ) <sup>a</sup>	angles $a_1\text{--}a_6$ <sup>a</sup>
ideal trigonal bipyramid <sup>b</sup>	53.1, 53.1, 53.1	101.5, 101.5, 101.5, 101.5, 101.5, 101.5
ideal square pyramid <sup>b</sup>	0.0, 75.7, 75.7	75.7, 75.7, 119.8, 119.8, 119.8, 119.8
$\{\text{VO}_5\}$ unit of ( <b>1</b> )	27.1, 50.9, 56.4	87.2, 87.4, 109.5, 111.6, 114.9, 118.6
$\{\text{VO}_5\}$ unit of ( <b>2</b> )	3.1, 86.0, 88.4	86.6, 89.4, 122.2, 124.6, 125.0, 126.5

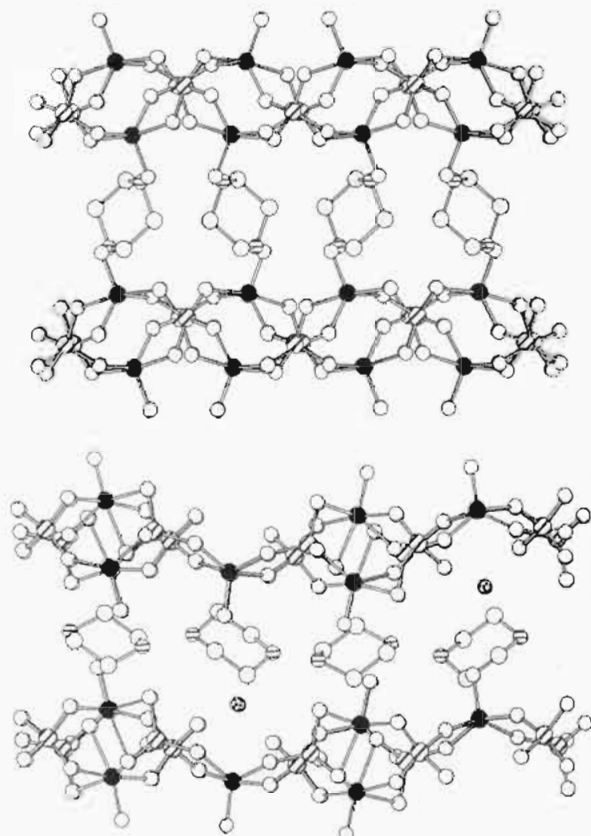
<sup>a</sup> Angles  $e$  and  $a$  are as described in ref 26. <sup>b</sup> Values are from ref 26. run parallel to **b**, as shown in Figure 3a. The interlayer region, which exhibits an atom to atom (O1...O1) distance of 7.8 Å, is occupied with piperazinium dications. The layers are hydrogen bonded to the cation, as suggested by N1-O1 distances of 2.98 Å.

In contrast, compound **2** has V/P/O layers constructed from  $\text{VO}_6$  octahedra,  $\text{VO}_5$  square pyramids, and  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$  tetrahedra. The five-coordinate vanadium site V3 exhibits the common square-pyramidal geometry with the basal positions defined by oxygen donors from each of four adjacent phosphate groups and the apical position by the terminal oxide group. As

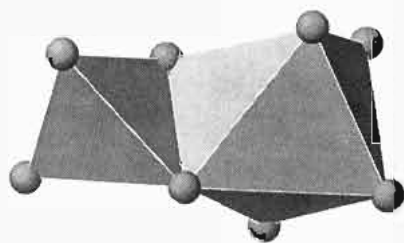
(26) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* 1974, 96, 1748.

(27) Brown, I. D. *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol II, pp 1-30.





**Figure 3.** (a, top) View of **1** down *c*. Atoms are depicted in the following way: vanadium, black circle; phosphorus, diagonally striped; oxygen of V–P–O layer, small open; carbon, gray; nitrogen, horizontally striped. (b, bottom) View of **2** down [010], showing the organic and inorganic layers. Same atom-coding scheme as part a, with the addition of dotted circles to represent the oxygen of the water molecule.



**Figure 4.** Polyhedral representation of the edge sharing  $\text{VO}_6$  octahedron and the phosphate tetrahedron of **2**.

indicated by the values listed in Table 6, the geometry of this vanadium center closely approximates the idealized square pyramidal limit. In contrast, V1 and V2 exhibit highly distorted octahedral geometries. The  $\{\text{VO}_6\}$  polyhedra associated with these centers are defined by three oxygen donors from each of three adjacent phosphates, the terminal oxide group and two oxygen donors from a bidentate phosphate unit. This edge-sharing interaction between  $\{\text{VO}_6\}$  and  $\{\text{PO}_4\}$  polyhedra, shown in Figure 4, is unique in the chemistry of solid V/P/O phases and represents an additional variable in polyhedral connectivities which further expands the structural possibilities for such phases. While there are three crystallographically independent vanadium sites in two distinct geometries, valence sum calculations<sup>27</sup> give values of 3.90–4.05 valence units, confirming that all vanadiums are in the +4 oxidation state.

The  $\{(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2\}$  layer composition of **2** gives a V/P ratio of 3/4, which may be contrasted to a V/P ratio of 1/1 in  $\text{VOPO}_4$ . This feature generates a missing octahedral site in the  $\text{MOPO}_4$  layer giving rise to the vacancies illustrated in Figure 2c. A concomitant consequence of this “defect” is the edge-sharing interaction between polyhedra referred to previously.

**Table 7.** Selected Contact Distances (Å) for the Structures of  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_2(\text{PO}_4)_2]$  (**1**) and  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2[(\text{VO})_3(\text{HPO}_4)_2(\text{PO}_4)_2] \cdot \text{H}_2\text{O}$  (**2**)

	<b>1</b>		<b>2</b>
N1–O1	3.01(1)	O15–O11	2.79(1)
N1–O3	2.88(1)	O15–O19	2.76(1)
N1–O4	2.79(1)	O15–O20	2.83(1)
		O19–O20	2.82(1)
		N1–O1	2.92(1)
		N1–O8	2.75(1)
		N2–O2	2.93(1)
		N2–O17	2.89(1)

Charge considerations require protonation of the remaining phosphate groups. In contrast to the layers in **1**, those in **2** undulate so as to produce proximal and distal distances between the layers, resulting in two crystallographically different piperazinium dications. As in compound **1**, the vanadyl groups of **2** point toward the interlayer region and are hydrogen bonded to the piperazinium dications. The composition of **2** establishes the presence of one water molecule per formula unit, which is shown as dotted circles in Figure 3b. In common with structure **1**, appreciable hydrogen bonding occurs between the layers and the dications in **2** (Table 7).

Since layered solids have been studied extensively as inorganic ion exchangers,<sup>28</sup> preliminary exchange reactions were performed on compound **1** with piperidine and 1,4-diaminopiperazine hydrochloride. The former resulted in dark needles with the formula  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2(\text{H}_2\text{NC}_3\text{H}_{10})[\text{H}_4\text{PV}_{14}\text{O}_{42}]$ ,<sup>29</sup> whereas the latter gave a blue microcrystalline powder. The observation of a 2-D solid such as **1** dissociating into molecular units upon reaction with piperidine is most unusual. Experiments are under way to exchange the piperazinium dication with other organic cations and dications, so as to observe how these layers adjust to cations of different size, charge, and hydrogen-bonding requirements.

## Conclusions

Hydrothermal synthesis affords a convenient preparative technique for the isolation of complex, metastable inorganic materials from simple precursors. Appropriate manipulation of reaction conditions allows the incorporation of different organic templates into the interlamellar region between inorganic layers of two-dimensional solid V/P/O phases. While the existence of the templating effect is well established, the mechanism is not well understood. In the case of compounds **1** and **2**, minor changes in reaction conditions result in different structures incorporating the same template. The structural complexity of the V/P/O system reflects the variability of coordination number and oxidation state associated with vanadium, as well as the diversity of connectivity patterns which may be generated between a given vanadium polyhedral type and the various phosphate tetrahedra  $\{\text{H}_n\text{PO}_4\}^{(3-n)-}$  which may be present. While hydrothermal synthesis affords some control over the outcome of solid-state reactions, the assembly of a material of desired geometry remain an elusive goal.

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**Supplementary Material Available:** Tables of crystal data, experimental conditions, atomic positional parameters, bond lengths and angles and anisotropic temperature factors for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

(28) Alberti, G. *Acc. Chem. Res.* **1978**, *11*, 163. Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(29)  $(\text{H}_2\text{NC}_4\text{H}_8\text{NH}_2)_2(\text{H}_2\text{NC}_3\text{H}_{10})[\text{H}_4\text{PV}_{14}\text{O}_{42}]$ : monoclinic space group  $C2/c$  with  $a = 19.246(2)$  Å,  $b = 20.894(4)$  Å,  $c = 13.344(2)$  Å,  $\beta = 110.29(1)^\circ$ ,  $V = 5033(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 2.22$  g cm<sup>-3</sup>; structure solution and refinement based on 1677 reflections with  $I_0 \geq 3\sigma(I_0)$  converged at  $R = 0.0648$ . The structure of the anion is identical to that previously reported for  $(\text{Me}_3\text{NH})_4(\text{NH}_4)[\text{H}_4\text{PV}_{14}\text{O}_{42}]$ .<sup>30</sup>

(30) Khan, M. I.; Zubietta, J.; Toscano, P. *Inorg. Chim. Acta* **1992**, *193*, 17.